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(54) Method of treating aqueous process liquors

(57) A process for treating aqueous process liquors, eg. in waste paper recycling, which contain catalase positive micro-organisms and thereby reducing the rate of hydrogen peroxide decomposition by catalase employs an organic peracid as a biocide with the process liquor at acidic or neutral pH. The pH is preferably from about 6 to 6.5, and controlled by use of a mineral acid which is preferably added in the same solution as the peracid. The peracid is preferably an aliphatic peracid having from 1 to 6 carbon atoms, and is most preferably peracetic acid. The liquor subsequently undergoes bleaching by hydrogen peroxide.

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Method of Treating Aqueous Process Liquors

This invention concerns methods for treating aqueous process liquors. More specifically, this invention concerns methods for treating aqueous process liquors, and particularly aqueous process liquors in the paper industry.

The production of paper at paper mills often involves the production of an alkaline paper pulp. During such a pulping process, the pulp can develop an undesirable yellow colouration which often detracts from the value of the paper finally produced. To ameliorate this problem, it is often desirable for the aqueous process solution to be treated with hydrogen peroxide to bleach the pulp, and it is therefore advantageous, for example, in terms of process costs, that there is efficient usage of the hydrogen peroxide.

One of the factors which can reduce the efficiency of hydrogen peroxide usage is the presence of the enzyme catalase in the process liquors. This enzyme serves to decompose hydrogen peroxide, thus reducing the amount available for bleaching the pulp. The principal source of catalase in aqueous process liquors are micro-organisms, which produce catalase as part of their metabolism and as part of their defence mechanism when the micro-organism is contacted with solutions containing hydrogen peroxide. The problems of inefficient hydrogen peroxide usage caused by the presence of catalase are particularly prevalent where the paper mill is producing paper from recycled waste paper.

The aqueous process liquors provide an environment which is suited to the growth of many species of micro-organism, and this problem is exacerbated by the extensive recycling of these liquors in order to improve chemical usage and reduce water consumption and effluent discharges. This allows the population

of micro-organisms to reach a much higher level than if the process liquors were not recycled.

The problem of the production of catalase is further exacerbated by the hydrogen peroxide concentrations in the pulping liquors being sufficient to kill the micro-organisms which do not produce catalase or produce only a relatively small amount of catalase, so-called catalase negative organisms, but not to reduce significantly the numbers of micro-organisms which produce a relatively large amount of catalase, so-called catalase positive organisms. This reduces the competition for nutrients faced by catalase positive organisms, and this means the population of micro-organisms in the pulping liquors consists mainly of catalase positive organisms rather than a mixture, and so the quantity of catalase produced in the solutions is increased. The higher levels of catalase produced cause more rapid decomposition of the hydrogen peroxide and thus can have a detrimental effect on the efficiency of the hydrogen peroxide usage.

It is therefore expedient to reduce the numbers of catalase positive organisms in pulping liquors, and previous proposals for this have principally involved the use of organic biocides such as methylene bis thiocyanate or one or more dithiocarbamates, or the use of catalase inhibitors such as hydroxylamine. However, in recent years, there has been increasing concern about the toxicity of certain organic biocides, and their effect on the environment, and so investigations have been made to identify suitable biocidal systems which are of a low order of toxicity and which have a low impact on the environment.

It is beneficial for both cost and space reasons that any treatment process to reduce the numbers of catalase positive organisms can be incorporated within the framework of an existing pulp stream without the need to construct expensive additional holding tanks and the like.

Accordingly, it is an objective of the present invention to provide a process for reducing the numbers of catalase positive organisms in aqueous process liquors, particularly the pulping liquors for waste paper recycling.

It is another objective of the present invention to provide a process for reducing the numbers of catalase positive organisms in aqueous process liquors, particularly the pulping liquors for waste paper recycling which employs a biocidal system of low order of toxicity and of low environmental impact.

It is yet another objective of the present invention to provide a process for reducing the numbers of catalase positive organisms in aqueous process

liquors, particularly the pulping liquors for waste paper recycling which can result in the reduction of the rate of decomposition of hydrogen peroxide in pulping liquors for waste paper recycling.

It is a further objective of certain embodiments of the present invention to provide a process for reducing the numbers of catalase positive organisms in aqueous process liquors, particularly the pulping liquors for waste paper recycling which can result in the reduction of the rate of decomposition of hydrogen peroxide in pulping liquors for waste paper recycling, said process being incorporated within the existing framework of a pulp stream without the need to construct expensive additional holding tanks and the like.

According to the present invention, there is provided a process for treating aqueous process liquors, characterised in that it comprises treating process liquors containing catalase positive micro-organisms at neutral or acidic pH with an organic peracid that has a disinfectant effect on the aqueous process liquor.

According to a second aspect of the present invention, there is provided a process for improving the stability of hydrogen peroxide introduced into an aqueous processing liquor, characterised in that it comprises treating the process liquors containing catalase positive micro-organisms at neutral or acidic pH with an organic peracid that has a disinfectant effect on the aqueous process liquor, and thereafter adjusting the pH of the process liquor to a pH effective for bleaching.

According to a third aspect of the present invention, there is provided a multistage process for the bleaching of aqueous pulp produced from recycled paper which includes a hydrogen peroxide bleaching stage, characterised in that in a peracid treatment stage the process liquors containing catalase positive micro-organisms are treated at neutral or acidic pH with an organic peracid that has a disinfectant effect on the aqueous process liquor, and thereafter the pH is optionally adjusted to a pH effective for bleaching, and hydrogen peroxide is introduced and maintained until the desired bleaching is obtained.

The organic peracid can be any organic peracid that has a disinfectant effect on the aqueous process liquor. However, in many embodiments, the organic peracid is selected from the group comprising aliphatic peracids containing from 1 to 6 carbon atoms. In most preferred embodiments, the peracid is peracetic acid.

The organic peracid in the process of the present invention is employed at an amount sufficient to reduce the numbers of catalase positive organisms present in the process liquors. It will be recognised that the amount of peracid required will depend to a large extent on the operating conditions of individual processes, for example, the liquor temperature or the contact time available for the peracid. In many cases, the concentration of peracid employed in the process liquors is greater than about 10ppm, often from about 40 ppm to about 1,000ppm, and most often is selected in the range from about 50ppm to about 250ppm. It will also be recognised that there will tend to be a reduction in the concentration of the peracid with time caused by the oxidative nature of the peracid.

In many instances, the process liquors are at alkaline pH thus necessitating reduction of the pH to neutral or acidic pH. It will be recognised by one skilled in the art that, although in theory it is possible to employ a pH of any value at or below 7, in practice, because the process liquors are subject to further processing which is conducted at a pH greater than 7, it is desirable to employ a pH of no lower than about 5, preferably no lower than about 6, and particularly preferably a pH between about 6 and about 6.5, as this reduces the amounts of acid and alkali needed to lower and raise the pH respectively.

The organic peracid is often conveniently supplied as an aqueous equilibrium solution comprising the peracid, the corresponding organic acid and hydrogen peroxide and optionally comprising one or more stabilisers to prolong the storage stability of the peracid. Such stabilisers well known for such conditions often comprise ethyleneaminopolymethylenephosphonic acids, or hydroxyethylidene diphosphonic acid or salts thereof and/or heterocyclic carboxylic acids such as dipicolinic or quinolinic acid in an amount of typically from about 0.001 to about 4% by weight.

An aqueous equilibrium solution of the organic peracid typically comprises from about 1% to about 45% by weight, preferably from about 5% to about 30% by weight organic peracid; from about 6% to about 60% by weight, preferably from about 10% to about 50% by weight of the corresponding organic acid and from about 5% to about 30% by weight, preferably from about 10% to about 25% by weight of hydrogen peroxide.

The peracid may be dosed manually into the process liquors, but in many embodiments, the dosing is automatically controlled by the use of a metering pump and a suitable control system which can deliver the peracid according to

a pre-determined programme, or in response to changes in the pH of the process liquors. The dosing can be carried out continuously while the process is operating, thereby maintaining a substantially low level of catalase positive micro-organisms, or may be carried out intermittently, such as at regular intervals throughout the operating period of the process, to reduce the population of catalase positive micro-organisms and thus prevent the growth of an excessive population.

It will be apparent that the peracid will reduce the pH of the process liquors to a certain extent because of its acidic nature, and indeed it is possible that the pH of the process liquors may be controlled to neutral or acidic pH by this method alone. However, it will also be recognised that peracids are normally relatively expensive, and that, as many organic acids and peracids are relatively weak acids, relatively large quantities are needed to significantly alter the pH and so it is preferable to control the pH by some other means. One convenient method is to employ a solution of one or more strong inorganic mineral acids such as sulphuric, phosphoric or nitric acid. Sulphuric acid is preferred because there is increasing environmental concern over the discharge of phosphate and nitrate in waste streams.

The mineral acid solution may be dosed into the process liquors either manually, or by the use of automatic pH control equipment which senses a change in the pH to above a predetermined value and doses the acid solution until the pH returns to the pre-set value. Such control equipment is well known in the art. In a preferred embodiment, the mineral acid is supplied in the same solution as the organic peracid, thus reducing the dosing equipment needed. When the mineral acid is dosed separately from the peracid, it will be recognised that the concentration may be varied considerably to suit the individual circumstances of the equipment and conditions of different processes, although the concentration of mineral acid in the solution is often conveniently in the range of from about 2 to about 25% by weight. When the mineral acid is contained in the same solution as the peracid, the mineral acid usually comprises greater than about 0.5% by weight, often from about 1% to about 15% by weight and most often from about 2% to about 10% by weight of the solution.

In advantageous embodiments of the present invention, the peracid and mineral acid are supplied in the same solution, and the solution is automatically dosed to the process liquors by a dosing system which is set to adjust the

process liquors to a pre-set pH during the peracid treatment, such as a pH from about 6 to about 6.5. The solution employed in these embodiments typically comprise the peracid and the mineral acid in a mole ratio of from about 1.5 : 1 to about 4 : 1 peracid : mineral acid, preferably in a mole ratio of from about 2 : 1 to about 3.5 : 1 peracid : mineral acid.

The peracid treatment can be carried out in a number of different ways. In one set of embodiments, the peracid is fed directly into a pipeline in which the process liquor is flowing. In another set of embodiments, the liquor is introduced into a holding tank, preferably dimensioned to achieve a desired residence time. In both sets of embodiments, the pH detector is located within the liquor.

In those embodiments where the treatment occurs in a flowing system such as a distribution pipe, the pH detector and the solution feed can be located at the same location or the pH detector can be located downstream of the solution feed.

In those embodiments where the treatment occurs in a holding tank, the solution feed is preferably located in the vicinity of the process liquor inlet to ensure that both the maximum peracid concentration is delivered to what is likely to be the most contaminated area, and the peracid is evenly distributed by the flow of the process liquors.

The stages of the process according to the present invention can be carried out over a wide range of temperatures, but in many cases the temperature is unlikely to exceed 90°C, or be lower than 5°C. In the majority of cases, the temperature will be between 10°C and 75°C, preferably between 30°C and 50°C. Heating means can be employed to heat the liquor, but in many embodiments, the temperature of the liquor is suitable without adjustment. Tanks and pipes containing the liquor can be lagged in order to maintain the temperature in the desired range.

In many embodiments, the treatment time for the peracid will usually be greater than about 5 minutes, and is unlikely to be longer than about 200 minutes. In many instances, the treatment time will be between 10 minutes and 100 minutes.

In a particularly preferred embodiment, the process according to the present invention comprises treating the aqueous process liquors with an initial concentration of about 50ppm to about 250ppm of peracetic acid, the peracetic acid being supplied as a solution containing 5% to about 30% by

weight peracetic acid, from about 10% to about 50% by weight of acetic acid, from about 10% to about 25% by weight of hydrogen peroxide and from about 2% to about 10% by weight of sulphuric acid, the mole ratio of peracetic acid to sulphuric acid being from about 2 : 1 to about 3.5 : 1. The treatment is effected at a temperature between 30°C and 50°C and the treatment period is between 10 minutes and 100 minutes.

The peracids can conveniently be prepared by mixing the corresponding acid with hydrogen peroxide in aqueous solution, in the presence of any desired stabilisers, at a temperature in the region of from 10°C to about 50°C and allowing to reach equilibrium. It is known in the art that the formation of an equilibrium solution of a peracid is catalysed by strong acids, and so in a particularly preferred embodiment, when the pH of the process liquors is to be controlled using a combined solution of the mineral acid and the peracid, it is particularly advantageous to employ the mineral acid as a catalyst to reduce the time to equilibrium of the peracid solution. It will be recognised that there are many alternative routes to the production of peracid solutions, and that it is possible for these methods to be employed to produce peracid solutions suitable for use in the present invention.

After the peracid treatment, the process liquors are normally passed to a hydrogen peroxide-based bleaching stage, where the pH can be adjusted to in the range of about 9 to 13 using a suitable alkali, for example sodium hydroxide. By virtue of the preceding peracid treatment, the population of catalase positive micro-organisms in the liquors will be substantially reduced thereby improving the stability of the hydrogen peroxide.

In many embodiments, the peracid treatment and hydrogen peroxide bleaching form part of an integral process loop in which process liquor is subsequently recycled after recovery of paper pulp from the liquors, and it is often these subsequent stages that allow the concentration of catalase positive micro-organism to increase to the extent that the stability of the hydrogen peroxide is detrimentally affected.

Having described the invention in general terms, embodiments of the invention will now be described more fully by way of example only.

Examples.

Example 1. Use of Peracetic Acid as a Biocide.

Samples of a pulper feed liquor were treated with 0, 50ppm, 100ppm and 200ppm of peracetic acid at room temperature for 10 minutes. The number of colony forming units per cm^3 in each of the samples was determined by adding 1 cm^3 of the sample to 9 cm^3 of sterile 1/4 Ringer solution containing $0.2cm^3$ of a solution of 0.25% w/v catalase and 5% w/v sodium thiosulphate as deactivator for excess peroxygen. Further serial dilutions in sterile 1/4 Ringer solution were made, then $1cm^3$ aliquots were plated with tryptone soya agar and incubated at 37°C for 48 hours, and then the plate count determined.

The results of the plate counts showed that the sample treated with 0ppm peracetic acid had 1.8×10^7 cfu/cm^3, that treated with 50ppm peracetic acid 3.9×10^2 cfu/cm^3, that treated with 100ppm peracetic acid 3.2×10^2 cfu/cm^3, and that treated with 200ppm peracetic acid 1.5×10^2 cfu/cm^3.

The results show that peracetic acid is an effective biocide for reducing the microbial count in aqueous process liquors.

Example 2. Reduction of Rate of Hydrogen Peroxide Decomposition.

6 samples of water from a commercial paper recycling mill known to contain high levels of catalase positive organisms and having a pH of 7.7 were treated with two different peracetic acid solutions of the compositions given in Table 1 below at room temperature for 15 minutes. Both solutions were employed at each of 50, 100 and 200ppm. The pH of the solutions were measured initially, and the concentration of peracetic acid measured using Merkoquant 10084 test strips for peracetic acid, commercially available from Merck, at intervals throughout the treatment. The 6 solutions were then treated with 100ppm hydrogen peroxide, and the concentration of the hydrogen peroxide in each sample monitored over 30 minutes using Merkoquant 10011 test strips for hydrogen peroxide, commercially available from Merck. The results are given in Table 2 below.

Table 1. Peracetic acid Compositions employed. (all % w/w)

Solution	% Peracid	% H_2O_2	% Acetic Acid	H_2SO_4
A	15	14	28	-
B	15	14	28	5

Table 2. Results of Treatment with Peracetic acid and Hydrogen Peroxide (All Concentrations are expressed as ppm)

Sample No	1	2	3	4	5	6
PAA solution	A	A	A	B	B	B
Initial pH	7.8	7.2	6.9	7.2	6.9	6.4
[PAA] @ t=0	50	100	200	50	100	200
[H_2O_2] @ t=0	100	100	100	100	100	100
" @ t=5 min	>25	>25	>25	>25	>25	>25
" @ t=20 min	20	20	>25	20	>25	>25
" @ t=25 min	10	10	15	10	15	20
" @ t=30 min	0	0	0	0	2	5

Comparing the results for samples 3, 5 and 6 (according to the present invention) with those for samples 1, 2 and 4 (not according to the present invention), it can clearly be seen that the rate of decomposition of hydrogen peroxide is significantly slower when the pH of the liquor being treated is less than pH 7, allowing the presence of a higher, more effective concentration of hydrogen peroxide to remain in the liquors, thus improving the process efficiency. A comparison of the results for samples 3 and 5 illustrate the benefit of the use of a mineral acid to control the pH. Both samples gave very similar results in terms of hydrogen peroxide stability, but it can be seen that only 100ppm of peracetic acid solution was needed to produce this benefit when the peracetic acid solution also contained 5% sulphuric acid, compared to 200ppm of peracetic acid when there was no sulphuric acid present. The use of a mineral acid can therefore be seen to allow a significant reduction in the peracid usage, and hence a cost saving for the process.

Claims.

1. A process for treating aqueous process liquors, characterised in that it comprises treating process liquors containing catalase positive micro-organisms at neutral or acidic pH with an organic peracid that has a disinfectant effect on the aqueous process liquor.

2. A process for improving the stability of hydrogen peroxide introduced into an aqueous processing liquor, characterised in that it comprises treating the process liquors containing catalase positive micro-organisms at neutral or acidic pH with an organic peracid that has a disinfectant effect on the aqueous process liquor, and thereafter adjusting the pH of the process liquor to a pH effective for bleaching.

3. A multistage process for the bleaching of aqueous pulp produced from recycled paper which includes a hydrogen peroxide bleaching stage, characterised in that in a peracid treatment stage the process liquors containing catalase positive micro-organisms are treated at neutral or acidic pH with an organic peracid that has a disinfectant effect on the aqueous process liquor, and thereafter the pH is optionally adjusted to a pH effective for bleaching, and hydrogen peroxide is introduced and maintained until the desired bleaching is obtained.

4. A process according to any of claims 1 to 3, characterised in that the organic peracid is dosed at an initial concentration of greater than about 10 ppm.

5. A process according to claim 4, characterised in that the organic peracid is dosed at a concentration of from about 40 ppm to about 1000 ppm.

6. A process according to claim 4, characterised in that the organic peracid is dosed at a concentration of from about 50 ppm to about 250 ppm.

7. A process according to any preceding claim, characterised in that the organic peracid is dosed as an aqueous equilibrium solution comprising the peracid, the corresponding acid and hydrogen peroxide.

8. A process according to any preceding claim, characterised in that the pH is adjusted to about pH 5 to 7.

9. A process according to claim 8, characterised in that the pH is adjusted to a pH between from about pH 6 to 6.5.

10. A process according to any preceding claim, characterised in that the pH is adjusted by the use of one or more mineral acids selected from the group consisting of sulphuric, phosphoric and nitric acids.

11. A process according to claim 10 characterised in that the mineral acid used to control the pH is a component of an aqueous equilibrium solution of peracid.

12. A process according to claim 11 characterised in that the mineral acid is present in the aqueous equilibrium solution of peracid at a concentration of greater than 0.5% by weight.

13. A process according to claim 12 characterised in that the mineral acid is present in the aqueous equilibrium solution of peracid at a concentration of from about 1% to about 15 % by weight.

14. A process according to claim 12 characterised in that the mineral acid is present in the aqueous equilibrium solution of peracid at a concentration of from about 2% to about 10 % by weight.

15. A process for treating aqueous process liquors containing catalase positive micro-organisms substantially as disclosed herein with reference to any one of Examples 3, 5 or 6.

17. A process for treating aqueous process liquors containing catalase positive micro-organisms substantially as described herein with respect to any novel feature or combination of features.

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Examiner's report to the Comptroller under Section 17 (The Search Report)

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Relevant Technical fields

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Search Examiner

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Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES: WPI

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27 SEPTEMBER 1993

Documents considered relevant following a search in respect of claims 1-15

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X,E	EP 0535741 A1 (INTEROX) see whole document	1,8,9
X	US 4548674 (HAGEMAN) see whole document	1,8,9
X	US 4400237 (KRUGER) see whole document	1,2,3,8,9

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

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